Research title: Investigation of high-T_c superconductivity in carbon nanotubes

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Background

Superconductivity, in which resistance of material drops to zero ohm and Meissner effect appears at a finite transition temperature (Tc), is one of the most exciting and attractive quantum phenomena. It has attracted high attention from academic, industrial, and ordinal people's societies. Realization of room-temparatue superconductivity is a dream of human being.

Various kinds of superconductors (SCs) have been discovered to date; e.g., CuO_2-based SC with high-T_c over 100K, SC metals (e.g., MgB_2 with T_c of 40K), organic SCs, etc.). Here, carbon nanotubes (CNTs) is nano-sized diameter tubes consisting of carbon atoms. After its discovery by Dr. Sumio Iijima at 1991, various unique structures, electronic states, and quantum phenomena have been reported. Application of CNTs is also actively studied. However, superconductivity in CNTs was not found before our discovery at 2006. We reported Tc of 12K for resistance drops to zero ohm in entirely end-bonded CNTs at 2006. Then, at 2008, we reported Tc of 12K for Meissner effect in boron-doped CNTs. Because it had been suggested that superconducting transition of CNTs is very difficult because of its one dimensionality, they gave strong impact to all societies. However, the Ts is still as low as 12K. In the present research program, we have carried out improvement of this Tc toward 30K.

Experimental and discussion

CNTs were synthesized by laser beam irradiation to cobalt catalyst including foreign atoms and vaporized them. We have synthesized CNTs with doping of various foreign atoms (boron, surfer, etc.). The foreign atoms were automatically doped into honeycomb-like carbon lattice of CNTs during growth by laser beam irradiation. Concentration of foreign atoms was controlled for 0 – 10 atomic % in the catalyst.

After synthesis, we performed very careful centrifuge and ultra-sonication of the CNTs in order to remove defects and impurities as much as possible. Then, a large volume of the CNTs was integrated to thin film structures. We carried out annealing of the CNTs under high vacuum (10^{-6} Torr) at high temperature (800 – 1200℃) for long time (1 day) in order to activate foreign atoms and form chemical bonds with carbon atoms. Absence of defects and impurities in the films were confirmed by observation of field-emission scanning electron microscopy (FESEM).

Magnetization of the thin films of CNTs were carefully measured by superconducting

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14. ABSTRACT
The magnetization of thin films of carrier-doped CNTs was measured. Increase in transition temperature Tc to 28 K was obtained by annealing the sample at 1473 K, which is higher than previous conditions. However, diamagnetism in zero-field-cooled and field-cooled regimes in raw data was not observed owing to positive background magnetization arising from residual impurities in CNTs. Hence, Meissner effect was not concluded in the present experiments. It is expected that further purification of the CNTs must realize confirmation of Tc = 28 K, as Meissner effect, and it may make Tc > 30K possible in the near future.

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Carbon nano tubes, Superconducting Materials

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quantum interference devices (SQUID; Quantum design) at T=2K – 60K. Meissner effect was identified by observation of appearance of diamagnetism in both zero-field cooling (ZFC) and FC regimes for temperature dependence of magnetization, and also observation of magnetic-field dependence of magnetization values at T=2K.

Results

Some typical features of magnetization are shown as below. Figure 1 shows temperature dependence of magnetization in boron-doped CNTs (boron concentration in catalyst 1.5 atomic %) annealed at 800℃, which is the same condition as previous one. In Figs.1(a) and (b), significant magnetization drops are observed at critical temperatures of 8K and 10K, respectively, in ZFC regime. Unfortunately, diamagnetism doesn't appear even at T = 2K in both figures. However, the critical temperatures of 8K and 10K for significant magnetization drops are very close to the highest T_c of 12K found in our boron-doped CNTs. Thus, these magnetization drops can be due to possible Meissner effect. Positive background magnetization owing to residual impurities in CNTs still obstructs observation of diamagnetism. Moreover, in FC regime, no magnetization drop is observed in Fig.1. This is also attributed to residual impurities. Although we removed impurities as much as possible by centrifuge and ultra sonication, it is difficult to remove them completely.

In contrast, Fig.2(a) shows the result of boron-doped CNTs annealed at 1200℃, which is higher than previous condition. Importantly, evident magnetization drop is observed as high as 28K in ZFC regime. This is the highest value compared with previous T_c of CNTs and also other SCs except for Fe- and CuO2-based SCs and fullerene-based SCs. Although magnetization drop is not observed in FC regime, we measured magnetization as a function of magnetic field. The result is shown in Fig.2(b). Evident hysteresis loop for diamagnetism is observed. It suggests a possibility that the magnetization drop in Fig.2(a) is attributed to Meissner effect. If this result is certainly Meissner effect, T_c of 28K must become extremely important in history of superconductivity. Therefore, further purification of the CNTs is indispensable.

Figure 3 shows temperature dependence of magnetization in sulfur-doped CNTs. The characteristics are very interesting. Magnetization values are in negative region (diamagnetism) at all temperatures < 50K and magnetization values start to drop from as high as 20K in ZFC regime. 20K is the highest value compared with previous reports including our publication, if it is T_c for Meissner effect. Moreover, much more significant magnetization drop is observable at 60K. These features are reproducible among different samples. However, because no magnetization drop is observable in FC regime.

we cannot conclude 20K as T_c for Meissner effect. Also in field-dependence of magnetization, diamagnetism was not observed. In order to confirm Meisener effect, impurities must be removed further. Origin of magnetization drop at 60K should be related to sulfur doping, because such phenomena has not been in CNTs with other impurities.

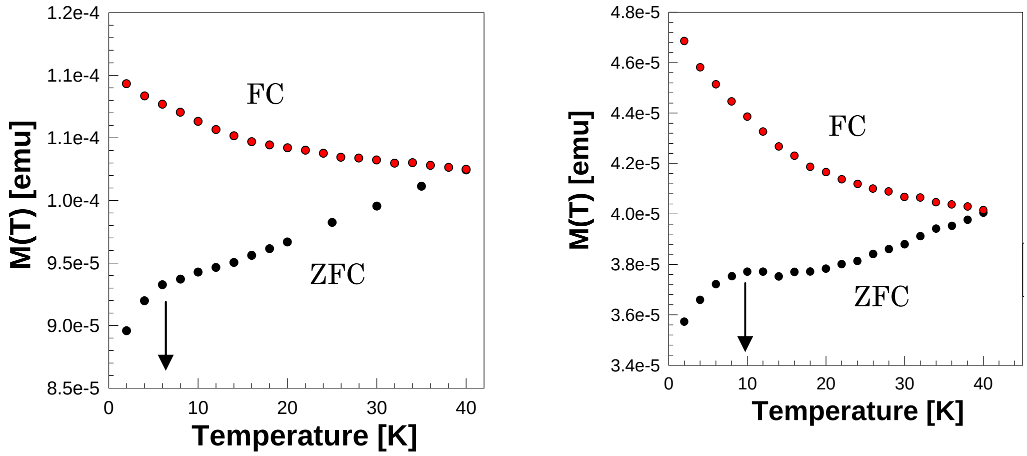

Fig.1: Magnetization as a function of temperature in two thin films of boron-doped CNTs annealed at 800℃ (<u>conventional condition</u>).

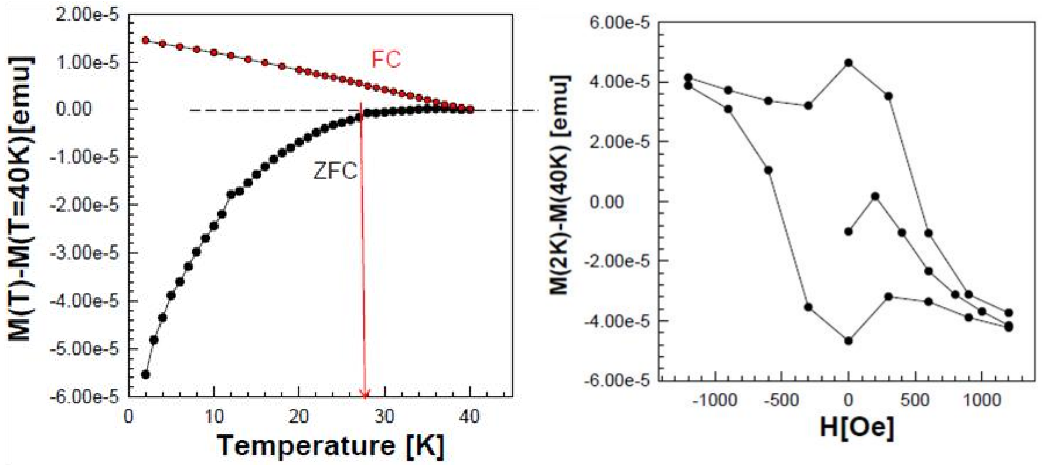

Fig.2: (a) Normalized magnetization as a function of temperature in a thin film of boron-doped CNTs annealed at 1200℃ (<u>novel condition</u>). (b) that as a function of magnetic field at 2K.

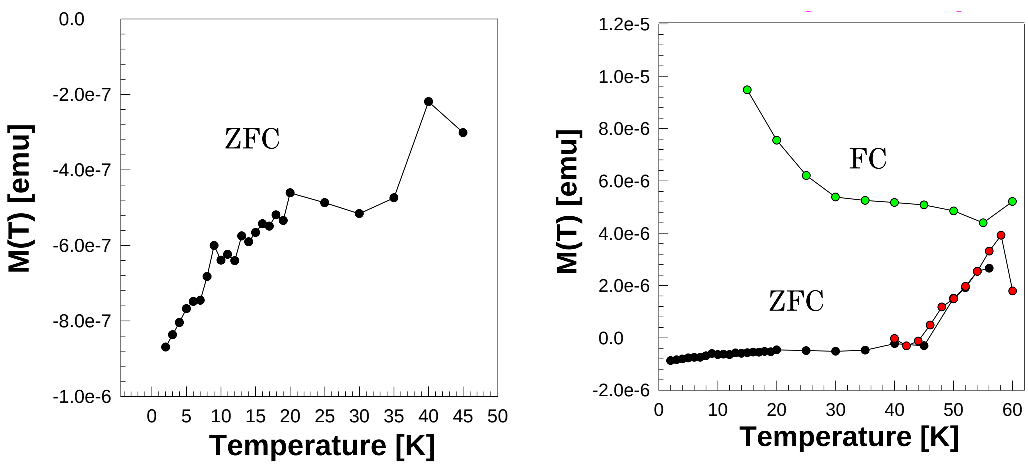

Fig.3: Magnetization as a function of temperature in a thin film of sulfur-doped CNTs annealed at 800℃. (a) T < 45K and (b) T < 60K.

Conclusion

We have measured magnetization of thin films of carrier-doped CNTs. Increase in Tc to 28K was obtained by annealing the sample at 1200℃, which is higher than previous conditions. However, diamagnetism in ZFC and FC regimes in raw data was not observed owing to positive background magnetization arisen from residual impurities in CNTs. Hence, Meissner effect was not concluded in the present experiments. It is expected that further purification of the CNTs must realize confirmation of Tc = 28K as Meissner effect and make Tc > 30K possible in near future.